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THE CuBr/Fe^0 PROMOTED RADICAL ADDITION OF METHYL 2-Br-2-Cl-CARBOXYLATES TO OLEFINS

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Abstract: Methyl 2-Br-2-Cl-carboxylates afford 2-alkyl-2-Cl-4-Br-carboxylates in fair yields by reaction with terminal alkenes, under mild conditions, through a radical process promoted by CuBr/Fe^0 in DMF/CH_2Cl_2.

The homolytic cleavage of carbon-halogen bonds giving rise to the radical addition of halogenated compounds to alkenes, is a well-known procedure to obtain C-C bonds.[1] Usually these reactions are initiated by organic peroxides,[2] transition metal salts or complexes,[3] or tributyltin hydride.[4] By the first two reagents a second, synthetically useful, functionality is introduced in the skeleton.[3]

Following the addition of methyl α-Br-esters to olefins,[5] carried out by Kharasch using diacetyl peroxide as initiator, a remarkable interest developed on the radical addition of α-haloesters to carbon-carbon double bonds; besides tin hydride or peroxides initiated methods,[6] metal catalyzed procedures were devised.[7]

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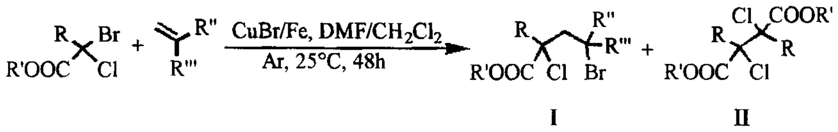
Whereas trihaloacetate esters[6,7] have been the preferred substrates, alkyl α,α-dihalocarboxylates have received little attention, restricted to the use of some dichloroacetates[8] or α,α-dichloro olefinic esters.[9] These reactions are assisted by transition metal salts or their complexes like CuCl,[8c] Cu(bpy)Cl,[8a-b] $RuCl_2(PPh_3)_3$,[8d-e,9] or $Fe(CO)_5$[8f] and require a long heating to 120-160°C, very likely to activate the C-X bond cleavage.

Here we report on the radical addition at 25°C of methyl 2-Br-2-Cl-carboxylates to alkenes promoted by the combinate CuBr/Fe.[10]

RESULTS AND DISCUSSION

After the finding that CuBr/Fe in dimethylformamide (DMF), at room temperature, efficiently promotes the radical homocoupling of methyl 2-Br-2-Cl-carboxylates,[11] we checked if these esters could undergo a Kharasch addition with 1-octene (Scheme 1). Starting from methyl 2-Br-2-Cl-hexanoate the addition product was obtained in low yield (Table 1, entry 1); on using a 1:1 mixture of DMF/CH_2Cl_2, which solubilizes completely the 1-octene, much better results were achieved (Table 1, entry 2).[12] Methyl 2-Cl-2-alkyl-4-Br-decanoates were thus prepared in fair yields from a number of methyl 2-Br-2-Cl-carboxylates, dimethyl α,α'-dichlorosuccinates being obtained as by-products. Only when resonance stabilized radicals (Table 1, entry 6) are expected the addition failes.[13, 15c]



Scheme 1

Table 1. Addition of Methyl 2-Br-2-Cl-Carboxylates to 1-Octene.

entry	R	R'	product yields (mol/mol %)[a]	
			adduct I	homocoupled II
1[b]	n-C_4H_8-	-CH_3	36	36
2	n-C_4H_8-	-CH_3	60	24
3	i-C_3H_7-	-CH_3	58	27
4	C_6H_5-CH_2-	-CH_3	48	18
5	CH_3-	-CH_3	62	20
6	C_6H_5-	-CH_3	-	43[c]
7	CH_3-	-CH_2-CH=CH_2	61	24

a) based on the ester; all products are 1:1 mixtures of diastereoisomers; b) reaction performed in DMF (1 ml/mmol of ester) alone and with 10 eq. of 1-octene; c) fumaric and maleic derivatives were also produced (30%).

In the case of allyl 2-Br-2-Cl-propanoate (Table 1, entry 7) inter- and intramolecular addition do not compete, the relatively low reaction temperature not allowing the intermediate radical to adopt the *anti* conformation required for cyclization.[14]

On reacting methyl 2-Br-2-Cl-propanoate with different olefins (Table 2) good results were only obtained with terminal alkenes, according to the well-known influence of sterical effects on radical additions.[7b,13,15] This is pointed out in the case of the 4-vinyl-cyclohexene (Table 2, entry 7), which chemospecifically reacts at the monoalkylated carbon-carbon double bond.

A C-2 alkyl substituent in the olefin favours the addition of the electrophilic carboxychloromethyl radical with respect to the homocoupling reaction (Table 2, entry 6), owing to the increased nucleophilicity of the carbon-carbon double bond;[1d] in this case, however, the separation of the Kharasch adduct is virtually impossible since it easy decomposes to a lot of products. With the allyltrimethylsilane derivative (Table 2, entry 9) the addition adduct β-bromoalkylsilane readily eliminates trimethylsilylbromide[16] affording methyl 2-butyl-2-Cl-but-3-enoate.

Table 2. Addition of Methyl 2-Br-2-Cl-Propanoate to Olefins.

entry	R''	R'''	product yields (mol/mol %)[a]	
			adduct I	homocoupled II
1	$CH_3(CH_2)_2CH_2$-	-H	65	19
2	CH_2=$CHCH_2CH_2$-	-H	66	15
3	$CH_3(CH_2)_4CH_2$-	-H	62	20
4	CH_2=$CH(CH_2)_3CH_2$-	-H	64	12
5[b]	$(CH_3)_3C$-	-H	35	40
6	$CH_3(CH_2)_2CH_2$-	$-CH_3$	50[c]	5[c]
7	4-cyclohexenyl	-H	58	18
8	C_6H_5-CH_2-	-H	60	20
9	$(CH_3)_3Si$-CH_2-	-H	64	12
10	CH_3-CO-O-CH_2-	-H	37	43

a) Based on the ester (all adducts I are 1:1 mixtures of diastereoisomers); b) Reaction time 72 h; c) GC yields.

From easy polymerizable substrates, like e. g. ethyl methacrylate, large amounts of oligomers are obtained.

Previously we rationalized the effectiveness of CuBr/Fe^0 in promoting the homolytic cleavage of C-Br bond of methyl 2-Br-2-Cl-carboxylates by the in situ formation of $FeBr_2$, produced by CuBr oxidation of Fe^0.[17] Since now no conversion has been detected when $FeBr_2$ is used alone, we discard it as the promoter of the C-Br bond breaking. On testing the other components of the system,[17] separately CuBr, Fe^0 and Cu^0, the Kharasch addition (Table 3, entries 2 and 3) occurred both with Fe^0 and Cu^0. Only Fe^0 can be however considered the real promoter since it gave almost the

Table 3. Addition of Methyl 2-Br-2-Cl-Hexanoate to 1-Octene with different metals.

entry	metal[a)]	conversion at 24h (%)	products yields (%)[b)]	
			adduct I	homocoupled II
1	Fe^0/CuBr	86	62	8
2	Fe^0	86	57	11
4	Cu^0	100	49	34
4	Mn^0	100	30	30
5	Co^0	9	4	0.3
6	Ni^0	10	6	0.4
7	Sn^0	100	1	73
8	Zn^0	100	12	23

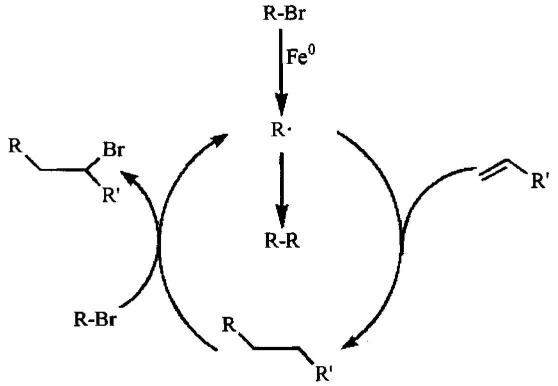
a) 1 mmol of metal/mmol of ester; b) GC yields.

same result of the CuBr-Fe^0 combinate, whereas Cu^0 showed poor chemoselectivity towards the addition reaction. The slightly better result with the couple CuBr/Fe^0 has to be likely attributed to the electrochemical activation of the iron surface.

Other transition metals were tested, affording, however, poor results in all cases (Table 3).

Oligomers formation from ethyl methacrylate suggests a conventional free radical chain addition (Scheme 2) rather than a redox-transfer chain mechanism.[7e,7i,8b] This hypothesis is also supported by the formation of some amounts of the addition product from 1-octene and methyl trichloroacetate, in a reaction mixture containing also methyl 2-Br-2-Cl-hexanoate. Methyl trichloroacetate is indeed unreactive towards CuBr/Fe^0 under the mild conditions used, but it can be involved in free radical chain addition.[6o]

Considering that polyhalocompounds, particularly those containing at least one bromine atom, easy accomodate extra electrons,[18a] initiation likely occurs at the metal



Scheme 2

surface by electron-transfer to the methyl 2-Br-2-Cl-carboxylates with concomitant expulsion of a bromide anion.[18b)] The high experimental ratio (5:1) between alkenes and haloesters agrees with of the easy chain termination by carboxy chloromethyl radicals homocoupling.

EXPERIMENTAL PART

Alkenes were standard grade commercial products and used without further purification. DMF and CH_2Cl_2 were dried over three batches of 3Å and 4 Å sieves (5% w/v, 12h), respectively. Fe^0 (fine powder) was purchased from Riedel-deHaen and $FeBr_2$ from Aldrich or prepared in situ by oxidation of Fe^0 with CuBr in DMF under inert atmosphere. Methyl 2-Br-2-Cl-carboxylates were prepared according to our previous procedure.[19] Mass spectra were obtained on a combined HP 5890 GC - HP 5989A MS Engine. ^1H NMR spectra were recorded on a Bruker WP80 spectrometer.

Preparation of methyl 4-Br-2-Butyl-2-Cl-decanoate. Iron powder (5 mmol) and CuBr (5 mmol) were weighted in a Schlenk tube, and then 1:1 DMF/CH_2Cl_2 (5 ml), 1-octene (25 mmol) and methyl 2-Br-2-Cl-hexanoate (5 mmol) were added under argon atmosphere. The mixture was stirred at room temperature, and after 48 h diluted with petroleum ether (b.p. 40-60°C) (10 ml) and filtered to remove residual Cu^0 and Fe^0. The filtrate was then washed with 5% HCl (2 x 5 ml), dried over Na_2CO_3 and evaporated. The products were isolated by chromatography on silica gel, using 1:9 diethyl ether/petroleum ether (b.p. 40-60°C) as eluant.

Methyl 4-bromo-2-butyl-2-chloro-decanoate

^1H NMR δ ($CDCl_3$): 0.7-1.05 (6H, 2 x $-CH_2-C\underline{H}_3$); 1.05-2.3 (16H, 8 x $-C\underline{H}_2-$); 2.4-2.9 (2H, m, $-C\underline{H}_2-CHBr$); 3.76 (3H, $-CO_2C\underline{H}_3$); 4.05-4.5 (1H, m, $-CH_2-C\underline{H}Br-CH_2-$). MS (EI, 70 eV) *m/z*: 298 (10%) [$M^+ - C_4H_8$]; 275 (78%) [M^+ - Br]; 239 (45%) [M^+ - Br - HCl]; 164 (83%) [$M^+ - C_8H_{15}Br$]; 55 (100%). Found: C, 50.7; H, 7.9%. $C_{15}H_{28}BrClO_2$ requires C, 50.64; H, 7.93%.

Methyl 4-bromo-2-chloro-2-isopropyl-decanoate

^1H NMR δ ($CDCl_3$): 0.7-1.15 (9H, $-CH_2-C\underline{H}_3$ and $-CH(C\underline{H}_3)_2$); 1.15-2.1 (10H, m, 5 x $-C\underline{H}_2-$); 2.4-3.9 (2H, m, $-C\underline{H}_2-CHBr$); 3.80 (3H, $-CO_2C\underline{H}_3$); 4.05-4.5 (1H, m, $-CH_2-C\underline{H}Br-CH_2-$). MS (EI, 70 eV) *m/z*: 298 (2%) [$M^+ - C_3H_6$]; 261 (63%) [M^+ - Br]; 225 (38%) [M^+ - Br - HCl]; 150 (93%) [$M^+ - C_8H_{15}Br$]; 41 (100%). Found: C, 49.1; H, 7.5%. $C_{14}H_{26}BrClO_2$ requires C, 49.21; H, 7.67%.

Methyl 2-benzyl-4-bromo-2-chloro-decanoate

^1H NMR δ ($CDCl_3$): 0.88 (3H, t, $-CH_2-C\underline{H}_3$); 1.05-2.1 (10H, m, 5 x $-C\underline{H}_2-$); 2.5-3.5 (4H, $-C\underline{H}_2-CHBr$ and $-C\underline{H}_2-C_6H_5$); 3.72 (3H, $-CO_2C\underline{H}_3$); 4.1-4.5 (1H, m, $-CH_2-C\underline{H}Br-CH_2-$); 7.25 (5H, bs, $-C_6\underline{H}_5$). MS (EI, 70 eV) *m/z*: 321 (2%) [M^+ - HCl - CH_3O]; 309 (1%) [M^+ - Br]; 273 (29%) [M^+ - Br - HCl]; 241 (7%) [M^+ - HBr - HCl - CH_3O]; 91 (100%). Found: C, 55.4; H, 6.6%. $C_{18}H_{26}BrClO_2$ requires C, 55.47; H, 6.72%.

Methyl 4-bromo-2-chloro-2-methyl-decanoate

^1H NMR δ ($CDCl_3$): 0.90 (3H, t, $-CH_2-C\underline{H}_3$); 1.1-1.95 (10H, m, 5 x $-C\underline{H}_2-$); 1.84 (3H, s, $-C\underline{H}_3$); 2.4-2.85 (2H, m, $-C\underline{H}_2-CHBr$); 3.78 (3H, $-CO_2C\underline{H}_3$); 3.95-4.35 (1H, m, -

CH_2-C<u>H</u>Br-CH_2-). MS (EI, 70 eV) *m/z*: 233 (35%) [M^+ - Br]; 197 (27%) [M^+ - Br - HCl]; 122 (100%) [M^+ - $C_8H_{15}Br$]. Found: C, 46.1; H, 7.0%. $C_{12}H_{22}BrClO_2$ requires C, 45.95; H, 7.07%.

Allyl 4-bromo-2-chloro-2-methyl-decanoate

^{1}H NMR δ ($CDCl_3$): 0.91 (3H, t, -CH_2-C<u>H</u>$_3$); 1.1-2.0 (10H, m, 5 x -C<u>H</u>$_2$-); 1.86 (3H, s, -C<u>H</u>$_3$); 2.45-3.07 (2H, m, -C<u>H</u>$_2$-CHBr); 3.95-4.4 (1H, m, -CH_2-C<u>H</u>Br-CH_2-); 4.5-4.8 (2H, m, -OC<u>H</u>$_2$-CH=CH_2); 5.1-5.55 (2H, m, -CH=C<u>H</u>$_2$); 5.65-6.25 (1H, m, -C<u>H</u>=CH_2). MS (EI, 70 eV) *m/z*: 281 (1%) [M^+ - C_3H_5O]; 259 (37%) [M^+ - Br]; 223 (8%) [M^+ - Br - HCl]; 148 (48%) [M^+ - $C_8H_{15}Br$]; 41 (100%). Found: C, 49.6; H, 7.0%. $C_{14}H_{24}BrClO_2$ requires C, 49.50; H, 7.12%.

Methyl 4-bromo-2-chloro-2-methyl-octanoate

^{1}H NMR δ ($CDCl_3$): 0.92 (3H, t, -CH_2-C<u>H</u>$_3$); 1.1-2.0 (6H, m, 3 x -C<u>H</u>$_2$-); 1.84 (3H, s, -C<u>H</u>$_3$); 2.45-2.85 (2H, m, -C<u>H</u>$_2$-CHBr); 3.80 (3H, -CO_2C<u>H</u>$_3$); 3.95-4.35 (1H, m, -CH_2-C<u>H</u>Br-CH_2-). MS (EI, 70 eV) *m/z*: 253 (2%) [M^+ - CH_3]; 225 (2%) [M^+ - $COOCH_3$]; 205 (38%) [M^+ - Br]; 169 (45%) [M^+ - Br - HCl]; 122 (93%) [M^+ - $C_6H_{11}Br$]; 109 (100%). Found: C, 42.2; H, 6.3%. $C_{10}H_{18}BrClO_2$ requires C, 42.05; H, 6.35%.

Methyl 4-bromo-2-chloro-2-methyl-7-octenoate

^{1}H NMR δ ($CDCl_3$): 1.7-2.45 (4H, m, 2 x -C<u>H</u>$_2$-); 1.83 (3H, s, -C<u>H</u>$_3$); 2.4-2.9 (2H, m, -C<u>H</u>$_2$-CHBr); 3.80 (3H, -CO_2C<u>H</u>$_3$); 4.0-4.35 (1H, m, -CH_2-C<u>H</u>Br-CH_2-); 4.85-5.25 (2H, m, -CH=C<u>H</u>$_2$); 5.5-6.1 (1H, m, -C<u>H</u>=CH_2). MS (EI, 70 eV) *m/z*: 203 (41%) [M^+ - Br]; 167 (38%) [M^+ - Br - HCl]; 122 (78%) [M^+ - C_6H_9Br]; 107 (100%). Found: C, 42.2; H, 5.6%. $C_{10}H_{16}BrClO_2$ requires C, 42.35; H, 5.69%.

Methyl 4-bromo-2-chloro-2-methyl-9-decenoate

^{1}H NMR δ ($CDCl_3$): 1.2-2.3 (8H, m, 4 x -C<u>H</u>$_2$-); 1.84 (3H, s, -C<u>H</u>$_3$); 2.35-2.85 (2H, m, -C<u>H</u>$_2$-CHBr); 3.80 (3H, -CO_2C<u>H</u>$_3$); 3.95-4.35 (1H, m, -CH_2-C<u>H</u>Br-CH_2-); 4.8-5.2

(2H, m, $-CH=C\underline{H}_2$); 5.5-6.1 (1H, m, $-C\underline{H}=CH_2$). MS (EI, 70 eV) *m/z*: 231 (38%) [M^+ - Br]; 195 (37%) [M^+ - Br - HCl]; 163 (100%) [M^+ - HBr - HCl - CH_3O]; 122 (70%) [M^+ - $C_8H_{13}Br$]. Found: C, 46.2; H, 6.6%. $C_{12}H_{20}BrClO_2$ requires C, 46.25; H, 6.47%.

Methyl 4-bromo-2-chloro-2,5,5-trimethyl-hexanoate

^1H NMR δ ($CDCl_3$): 1.06 (9H, s, $-C(C\underline{H}_3)_3$); 1.86 (3H, s, $-C\underline{H}_3$); 2.44-2.8 (2H, m, $-C\underline{H}_2-CHBr$); 3.79 (3H, $-CO_2C\underline{H}_3$); 3.86-4.2 (1H, m, $-CH_2-C\underline{H}Br-C-$); 5.68 (2H, m, $-CH_2-C\underline{H}=C\underline{H}-CH_2-$). MS (EI, 70 eV) *m/z*: 228 (6%) [M^+ - C_4H_8]; 205 (20%) [M^+ - Br]; 169 (32%) [M^+ - Br - HCl]; 122 (67%) [M^+ - $C_6H_{11}Br$]; 57 (100%). Found: C, 42.0; H, 6.2%. $C_{10}H_{18}BrClO_2$ requires C, 42.05; H, 6.35%.

Methyl 4-bromo-2-chloro-4-(4-cyclohexenyl)-2-methyl-butanoate

^1H NMR δ ($CDCl_3$): 1.4-2.3 (7H, m, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-C\underline{H}_2-$); 1.85 (3H, s, $-C\underline{H}_3$); 2.5-2.9 (2H, m, $-C\underline{H}_2-CHBr$); 3.80 (3H, $-CO_2C\underline{H}_3$); 4.05-4.4 (1H, m, $-CH_2-C\underline{H}Br-CH-$); 5.68 (2H, m, $-CH_2-C\underline{H}=C\underline{H}-CH_2-$). MS (EI, 70 eV) *m/z*: 277 (1%) [M^+ - CH_3O]; 229 (73%) [M^+ - Br]; 197 (23%) [M^+ - HBr - CH_3O]; 193 (43%) [M^+ - Br - HCl]; 161 (46%) [M^+ - HBr - HCl - CH_3O]; 133 (97%) [161 -CO]; 122 (60%) [M^+ - $C_8H_{11}Br$]; 79 (100%). Found: C, 48.9; H, 4.9%. $C_{13}H_{16}BrClO_2$ requires C, 48.85; H, 5.05%.

Methyl 4-bromo-2-chloro-2-methyl-5-phenyl-pentanoate

^1H NMR δ ($CDCl_3$): 1.80 (3H, s, $-C\underline{H}_3$); 2.3-3.35 (4H, m, $-C\underline{H}_2-CHBr-C\underline{H}_2-$); 3.76 (3H, $-CO_2C\underline{H}_3$); 4.15-4.5 (1H, m, $-CH_2-C\underline{H}Br-CH_2-$); 7.05-7.5 (5H, bs, $-C_6\underline{H}_5$). MS (EI, 70 eV) *m/z*: 239 (45%) [M^+ - Br]; 202 (55%) [M^+ - HBr - HCl]; 171 (33%) [M^+ - HBr - HCl - CH_3O]; 149 (100%) [171 -CO]; 91 (72%). Found: C, 46.4; H, 6.4%. $C_{12}H_{20}BrClO_2$ requires C, 46.25; H, 6.47%.

Methyl 2-chloro-2-methyl-4-pentenoate

^1H NMR δ ($CDCl_3$): 1.76 (3H, $-C\underline{H}_3$); 2.65-2.95 (2H, m, $-C\underline{H}_2-CH=CH_2$); 3.80 (3H, $-CO_2C\underline{H}_3$); 4.95-5.4 (2H, m, $-CH=C\underline{H}_2$); 5.5-6.2 (1H, m, $-C\underline{H}=CH_2$). MS (EI, 70 eV) *m/z*: 162 (1%) [M^+]; 127 (98%) [M^+ - Cl]; 126 (64%) [M^+ - HCl]; 95 (52%) [M^+ - HCl

- CH_3O]; 67 (100%) [95 -CO]. Found: C, 51.6; H, 6.7%. $C_7H_{11}ClO_2$ requires C, 51.70; H, 6.82%.

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